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10JAN03 E776030-1 D02776
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IP/P7083

2. Patent application number

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10 JAN 2003

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

QINETIQ NANOMATERIALS LIMITED

Registered Office 85 Buckingham Gate
London SW1E 6PD
United Kingdom

8540395001

GB

Patents ADP number (*if you know it*)

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

Improvements in and relating to ink jet deposition

5. Name of your agent (*if you have one*)

Ian Michael Johnson

"Address for service" in the United Kingdom to which all correspondence should be sent (*including the postcode*)QINETIQ LIMITED
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Description 8

Claim(s) 3

Abstract 1 *DML*

Drawing(s) 27

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DUPPLICATEImprovements in and relating to ink jet deposition

The present invention relates to a composition, method and apparatus for ink jet deposition, particularly, although not exclusively, of sub-micron sized structures.

5

It has been recognised that the materials processing and production techniques conventionally used in the manufacture of electrical, optical and mechanical components places a limitation upon their performance. In part, the limitation is believed to be attributed to the particulate size of materials from which such components are formed. Consequently, there has been much theoretical and practical work aimed at overcoming the performance disadvantages inherent in traditional materials processing and production techniques. In particular, there has been a concentration on the development of so-called nano-sized materials, that is materials whose particulate sizes are below one micron (<1μm).

15

Whilst some nano-sized materials have been prepared experimentally and are indeed available commercially in restricted quantities, the availability of suitable processing and production techniques remains a barrier to the full scale adoption of the technology. As a result, the anticipated benefits in terms of the improved performance characteristics of components manufactured using such materials are not being realised. By way of example, one such known manufacturing approach is that of photolithography. However, photolithography requires the use of lengthy, labour intensive processes and expensive patterning masks. A mask must be created for each application and/or device. As a result photolithography seems not to meet a primary commercial requirement of low cost.

It is also the case that in parallel with developments in the field of nano-material manufacture, there have been advances in the processes applied to the manufacture of components above the nano scale i.e. at the micron and greater scales. US 5,882,722 describes a thick film formed of a mixture of metal powders and metallo organic decomposition compounds in an organic liquid vehicle. The document also sets out a process for applying such a thick film to a substrate. However, the processes suggested in the document for applying such a film to a substrate such as screen printing, suffer from the disadvantages identified in general terms above. Another approach taken by those in the field has been that of ink jet printing in both so-called direct and indirect formats. Ink jet printing has applications as a deposition technique for materials consisting of particles greater than one micron in diameter

($>1\mu\text{m}$). Although direct ink jet printing is under investigation by some researchers, the structures which can be produced are very limited in terms of the type of materials which can be deposited and the accuracy of the structures which can be produced. Direct printing uses an ink containing a solid loading of the material to be printed, much in the same way that a graphical ink contains the required pigment. Alternatively a derivative of the required material, such as a salt, oxide or complex, can be used in suspension and printed, for later conversion to the required material. In some cases, it appears that there have been attempts even to utilise nano-sized materials in a direct ink-jet printing process. For example, US Patent No. 6,361,161 suggests that images may be produced using nano-sized particles. This Patent does not however suggest utilising such material for the creation of nanostructures. Furthermore, the approach taught in US Patent No. 6,361,161 is to utilise an ink made up purely of nanometric particles. For the most part, it is believed that the above described are some way from being commercially adopted, primarily, it is considered, owing to the difficulty in formulating a suitable ink.

Turning to indirect printing there has been much work directed at a particular deposition technique which has found favour in the production of structures as opposed to image formation. The process, which has similarities to an investment casting, is used to produce wax moulds within which a component is subsequently formed in a separate process. Such a process is long-winded and is not particularly suited to large-scale continuous production.

Thus, according to one aspect of the present invention, there is provided an ink composition for use with ink jet deposition apparatus, the ink composition comprising a solid loading having a particle size of less than one micron, a solvent, a dispersant or surfactant and a binder material wherein the ink is in a liquid state at ambient temperature.

Advantageously, by avoiding the need for a precursor material to generate the solid loading, a significant reduction in the complexity of material handling and processing is achieved. In particular, the complexities inherent in the conversion process in terms of the physical conditions and the like are obviated. The choice between a surfactant or a dispersant will depend on the nature of the interface which is to be formed between the constituents of the composition. A dispersant is, of course, capable of forming interfaces between solid and liquid phases only, whereas a surfactant can not only form interfaces between solid and liquid phases but also

between solid and solid, solid and liquid, solid and gas, liquid and liquid and liquid and gas phases.

Thus, according to another aspect of the present invention, there is provided a method of ink production, the method comprising homogenous mixing of a dispersant or surfactant and a solid loading having a particle size of less than one micron, followed by subsequent addition and homogenous mixing with a solvent carrier before addition of a binder and subsequent homogeneous mixing thereof.

According to a further aspect of the invention, there is provided a method of ink production, the method comprising homogenous mixing of a solvent and a solid loading having a particle size of less than one micron, followed by subsequent addition and homogenous mixing with a dispersant or surfactant before addition of a binder and subsequent homogeneous mixing thereof.

15

Advantageously the particulate size of the sold loading is known at the outset of the formulation process and is amenable to analysis. Unlike other methods, particularly those utilising precursor materials, this provides more confidence to those who might utilise such a composition in the production of tightly specified structures, for example.

In order to assist in understanding the invention, an embodiment thereof will now be described, by way of example, and with reference to the accompanying drawings, in which:

25 Figure 1 is a schematic diagram showing an ink jet printer for use with an ink in accordance with one aspect of the present invention;

Figure 2 is a schematic diagram showing a print head for use with the printer of Figure 1;

30 Figure 3 is a flow chart illustrative of a method of ink formulation in accordance with an aspect of the invention;

Figure 4 is a flow chart illustratiye of an alternative method of ink formulation in accordance with another aspect of the invention;

Figures 5a and 5b are respectively elevation and plan views of an example structure deposited using the ink of Figure 3 or Figure 4;

35 Figures 6a and 6b are respectively elevation and plan views of a further example deposited using the ink of Figure 3 or Figure 4; and

Figures 7a to 7d illustrate further examples of structures deposited using the ink of Figure 3 or Figure 4.

- Referring to Figure 1, there is shown an ink jet printer 1 under software control which
5 in this case is provided by a computer 2. The printer 1 is capable of delivering ink to a surface 3 of media 5 which in this case is a polymeric release film. The printer 1 is provided with a fixed bed 7 whilst each of a pair of print heads 9a,9b is capable of movement in the z-plane in addition to movement in the x and y plane. Each of the print heads 9 is of the piezo-electric type as exemplified by a commercially available
10 Siemens P2 print head. Clearly, it is envisaged that other ink jet deposition print heads may be utilised including not only those where the ejection of ink is brought about as a result of a piezo-electric distortion of an ink cavity but also print heads having thermal or shock wave based ejection mechanisms. The print heads 9 are fed by separate reservoirs 11a,11b to facilitate delivery of different inks without
15 having to repeatedly flush and refill each reservoir 11 and print head 9 more than necessary. Each print head 9 operates in accordance with a drop on demand process whereby ink is ejected by the print head 9 solely when it is required for deposition on a media surface.
- 20 Turning to Figure 2, this illustrates in more detail the print head 9 which includes a nozzle 13 of around 18 μm in diameter through which droplets of ink are ejected so as to impinge on the surface 3 of the media 5. Preferably, a print head 9 is selected with a nozzle diameter which provides the desired characteristics in both shape and volume of ejected ink. The composition and processing steps required to form an ink
25 suitable for printing with the printer 1 are described in detail below.

- Referring to the flowchart of Figure 3, an ink containing nano-sized particles, i.e. individual particles having a maximum dimension less than 1 μm , is formulated by firstly selecting 100 a solid starting material such as, but not limited to, a metal
30 powder, metal salts, metal oxides and ceramic material. Examples of metals include silver, silver/palladium and platinum whilst examples of ceramics include lead zirconate titanate, zirconia and alumina. The individual particles typically have a size in the range of 2 μm to 10nm.
- 35 To the starting material or solid loading as it may also be described, is added 102 a solvent carrier. Typically, the solvent carrier will contain between 5 and 60% by

volume starting material. The solvent carrier must be selected so that it will not destructively interfere with the print head 9 as a result of a chemical process and/or tribological action. Consequently, a solvent such as toluene or acetone should be avoided as should certain types of starting material which have a tribological impact, 5 unless, of course, such wear is deemed acceptable. Similarly, the starting material should be selected such that it does not exhibit electrostatic or Van der Waals forces which are sufficient to bring about agglomerations of the starting material which might interfere with the operation of the print head 9 through the formation of blockages, for example. The solvent should also be selected for its ability to wet the print head 9 10 and also with a view to defining the drying time of the ink once in contact with the media 5. The choice of an aqueous or non-aqueous solvent will, again, depend on the nature of the starting material. Examples of non-aqueous dispersants include ethyl-lactate and those which are alcohol based including combinations of ethanol and propan-2-ol, ethylene glycol and other alcohols. In the case of an aqueous 15 solution it has been found necessary to add a small amount of an alcohol such as ethanol to provide the wetting characteristics necessary to ensure the final ink composition is capable of wetting the print head 9.

In addition to the solvent, it has also been found advantageous to add 104 a 20 dispersant or a surfactant to the mixture of the solid material and solvent. It will be appreciated that a surfactant is particularly suitable, of course, for use with an aqueous solvent. The molecular structure of the dispersant or surfactant is such that each molecule has one end compatible with the material and another end which is compatible with the solvent. As a result, the dispersant or surfactant binds the 25 solvent to the material.

The resulting mixture is then homogenised 106 using a process such as milling. The process may be carried out for a number of hours. Typically, three hours is sufficient.

30 In an alternative embodiment of the present invention (see Figure 4), the dispersant or surfactant is added 200 to the starting material and both are mixed 202, typically the dispersant or surfactant is mixed by hand with the starting material. To the homogenised mixture is then added 204 sufficient solvent such that the starting material makes up between 5 to 60% by volume of the resulting mixture. The 35 resulting mixture may then homogenised 206, preferably through a further milling process for a matter of hours perhaps three hours.

It has also further been determined experimentally that in order to avoid cavitation or blockages within the nozzle 13, it is important to control the viscosity of the ink whilst it passes through the print head 9. Preferably, the viscosity of the ink will be in the range of 10-60cPs at ambient temperature. More preferably, the viscosity will be
5 selected to be in the range of 20-50cPs.

Typically, a manufacturer of a print head 9 will provide a range of viscosities which it is considered by the manufacturer are appropriate for an ink to be successfully deposited from the print head 9. Surprisingly, it has been found that inks in
10 accordance with present invention may still be printed successfully despite having a viscosity laying outside the range specified by the print head manufacture. It is believed that this is because the inks types considered by the manufacturer when determining the recommended viscosity range differ significantly in their desired characteristics from those of the present invention. To take one example, whilst
15 drying time is a significant attribute in relation to known inks suited for conventional printing operations, this is not the case with inks of the present invention where drying times may be much more extensive. In addition, the nature of the media 5 onto which the ink may be ejected from the print head 9 is also a factor in the selection of a viscosity or viscosity range for the ink. By controlling the viscosity of
20 the ink at the point of delivery to the medium 5 it is possible to optimise the shape and size of a drop of ink to meet the media requirements and to facilitate the build-up of a structure.

It has also been found experimentally that when multi-dimensional structures are built
25 up using an ink, a lack of physical integrity can arise in the built up structure unless steps are taken to control the integrity during the build of the structure.

With reference again to Figures 3 and 4, in order to address both of the above issues, it has been found useful to add 108,208 a further component to the
30 homogenised mixture, namely a binder. The type and quantity of binder added to the mixture of solvent, starting material and dispersant or surfactant is again determined by the required complexity of the built up structure and the factors determining the desired viscosity set out above. The binder itself has to be soluble in the selected solvent and also removable from the built up structure by a post printing process
35 such as leaching or firing, for example. Some suitable binders have been found to be polyvinylalcohol (PVA) and polyvinylbutyrol (PVB) for non-aqueous alcohol based solvents. Latex has been found to be a suitable binder for aqueous solvents.

The final step 110,210 in the preparation of the ink is to subject it to agitation in order to break down any tendency for the material to agglomerate. It has been found that ultrasonic techniques such as the use of an ultrasonic probe also known as a horn or

- 5 alternatively an ultrasonic bath are effective in breaking down any agglomerates. It is believed that the tendency for the starting material to agglomerate is due to Van der Waals forces which are interactions between closed-shell molecules and have contributions from interactions between the partial electric charges of polar molecules. Typically, the period required for ultrasonic agitation to achieve the result
10 of breaking down large scale agglomerations is up to five minutes or so, preferably around two minutes.

- It has been found useful to carry out such agitation 110,210 immediately prior to viscosity testing of the ink and also before utilising the ink in the deposition process
15 set out in more detail below.

- Once the ink has been agitated and any large agglomerations broken down, it has been found beneficial to use 112,212 the ink as soon as possible so as to minimise the opportunity for the material to agglomerate and a sediment to form.
20 Nevertheless, it has been determined that ink prepared in the above manner can be used at a later date provided agitation 110,210 is carried out to remove any sediment which has formed. It is expected that an ink formulated in the above described manner will become fully sedimented in no less than about six months. Accordingly, an ultrasonic probe 15 maybe incorporated in the reservoir 11 within the printer 1
25 itself, the agitated ink being subsequently delivered to the print head 9.

- In use, the reservoir 11 of the printer 1 is filled with ink prepared in accordance with the above procedure. The printer 1 itself, as has been mentioned, is capable of delivering ink to a medium 5 placed on the bed 7 at a particular position defined by
30 the x and y co-ordinates. Furthermore, because the bed 7 itself may be moved in the z direction it is possible to deposit ink onto the medium 5 at a number of x and y co-ordinates and at a fixed z position before displacing the bed 7 in the z direction and again depositing material at selected x and y co-ordinates. In this manner, it is possible to build up a structure 500 on the medium 5 having a three-dimensional
35 structure (Figures 5a and 5b). Clearly, a two dimensional structure 600 (Figures 6a and 6b) can be created by depositing the ink over the medium 5 with the bed 7 held in a fixed position relative to the print head 9.

- It will be recognised that control of each print head 9 and bed 7 may be placed under software control. Consequently, Computer Aided Design (CAD) software may be utilised to generate the design of a structure which can then be utilised in Computer Assisted Manufacture (CAM) of the structure by the printer. For example, the design of the structure may be created via a pixellated bit map. The software interprets the bitmap such that one pixel of the bitmap represents one ink drop. A three-dimensional structure may be built up by referring to a superimposed set of such bitmaps. This allows unique structures to be designed and produced on a drop by drop basis enabling complex geometries and hybrid structures to be realised.

Claims

1. An ink composition for use with ink jet deposition apparatus, the ink composition comprising a solid loading having a particle size of less than one micron, a solvent, a dispersant or surfactant and a binder material wherein the ink is in a liquid state at ambient temperature.
5
2. An ink composition as claimed in Claim 1, wherein between 5% to 60% of the volume of the ink comprises the solid loading.
10
3. An ink composition as claimed in Claim 1 or Claim 2, wherein the viscosity of the ink is in the range 10-60cPs at ambient temperature.
15
4. An ink composition as claimed in Claim 1 or Claim 2, wherein the viscosity of the ink is in the range 20-50cPs at ambient temperature.
20
5. An ink composition as claimed in any preceding Claim, wherein the solid loading remains substantially unsedimented for at least six months.
25
6. An ink composition as claimed in any preceding Claim, wherein the solid loading includes at least one of the following, namely a metal powder, a metal salt, a metal oxide and a ceramic material.
30
7. An ink composition as claimed in Claim 6, wherein the ceramic material is selected from at least one of the following, namely lead zirconate titanate, zirconia and alumina.
35
8. An ink composition as claimed in any preceding Claim, wherein the solvent is non-aqueous.
40
9. An ink composition as claimed in any one of Claims 1 to 7, wherein the solvent is aqueous.
45
10. An ink composition as claimed in Claim 8, wherein the solvent is an alcohol, a glycol, a lactate or a combination thereof.
50
11. An ink composition as claimed in Claim 9, wherein the binder is latex.
55

12. An ink composition as claimed in Claim 8, wherein the binder is PVA.
13. An ink composition as claimed in Claim 8, wherein the binder is PVB.
5
14. A method of ink production, the method comprising homogenous mixing of a dispersant or surfactant and a solid loading having a particle size of less than one micron, followed by subsequent addition and homogenous mixing with a solvent carrier before addition of a binder and subsequent homogeneous mixing thereof.
10
15. A method as claimed in Claim 14, wherein following the addition of the binder and the subsequent homogenous mixing thereof, ultrasonic energy is applied thereto.
15
16. A method as claimed in Claim 14 or Claim 15, wherein sufficient solid loading is added such that when mixed with the dispersant or surfactant it comprises between 5% to 60% by volume.
20
17. A method of ink production, the method comprising homogenous mixing of a solvent and a solid loading having a particle size of less than one micron, followed by subsequent addition and homogenous mixing with a dispersant or surfactant before addition of a binder and subsequent homogeneous mixing thereof.
25
18. A method as claimed in Claim 14, wherein following the addition of the binder and the subsequent homogenous mixing thereof, ultrasonic energy is applied thereto.
25
19. A method as claimed in any one of Claims 14 to 16 or Claims 17 and 18, wherein the solid loading is selected from at least one of the following, namely a metal powder, a metal salt, a metal oxide and a ceramic material.
30
20. A method as claimed in Claim 19, wherein the ceramic material is selected from at least one of the following, namely lead zirconate titanate, zirconia and alumina.
30
21. A method as claimed in any Claim appendent to Claim 14 or Claim 17, wherein a non-aqueous solvent is selected.
35
22. A method as claimed in any Claim appendant to Claim 14 or Claim 17, wherein the solvent is aqueous.

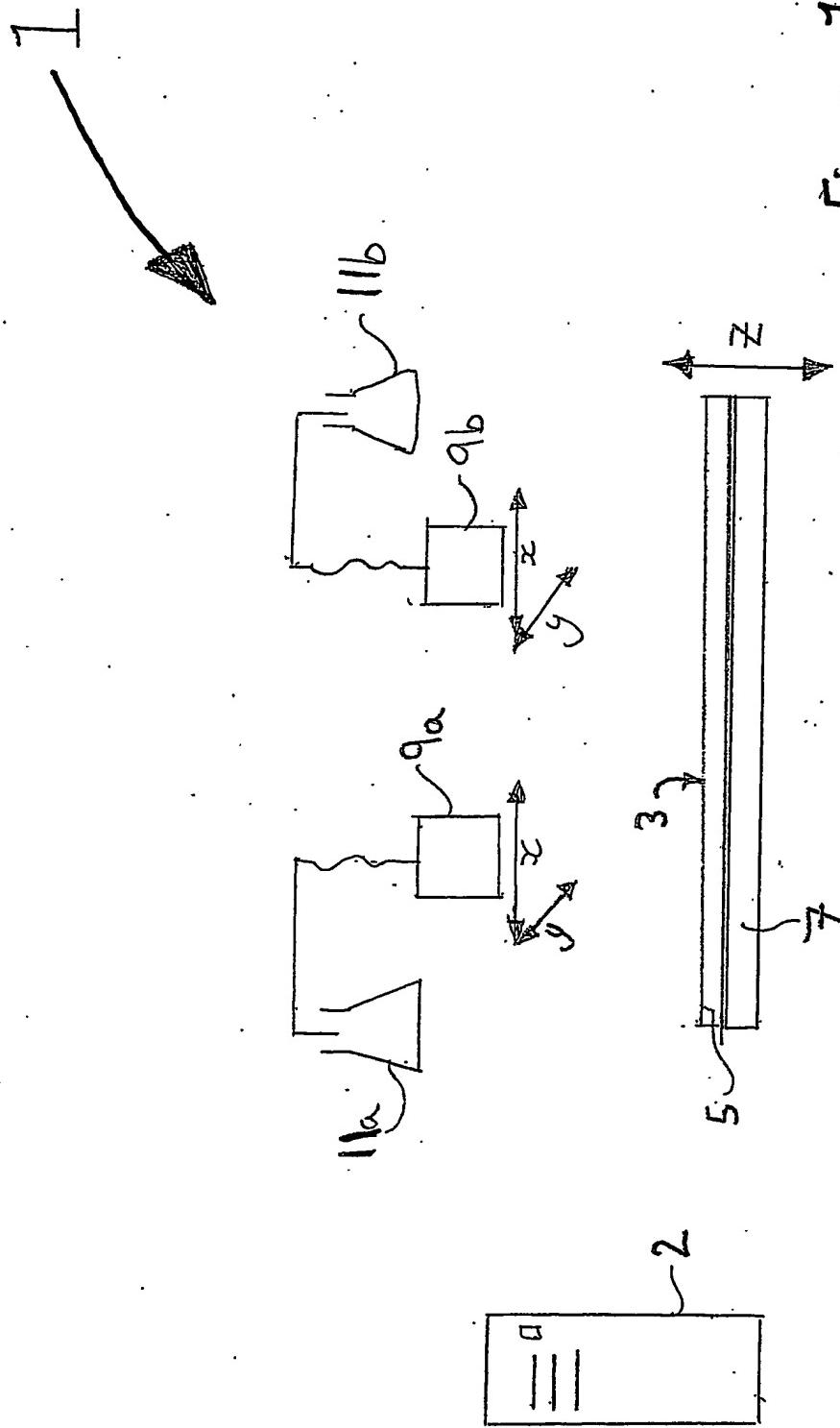
23. A method as claimed in Claim 21, wherein the solvent is selected from an alcohol, a glycol, a lactate or a combination thereof.
- 5 24. A method as claimed in Claim 22, wherein a wetting agent is added.

Abstract**Improvements in and relating to ink jet deposition**

- 5 An ink jet deposition technique utilises an ink formulation containing nano-sized material. The nano-sized material or loading is formulated to have an average particle size of less than one micron. The loading may comprise a metal powder, a metal salt, a metal oxide or a ceramic material. The ink formulation is particularly suitable in the deposition of complex small scale three dimensional structures.

Figure 1

1 of 7



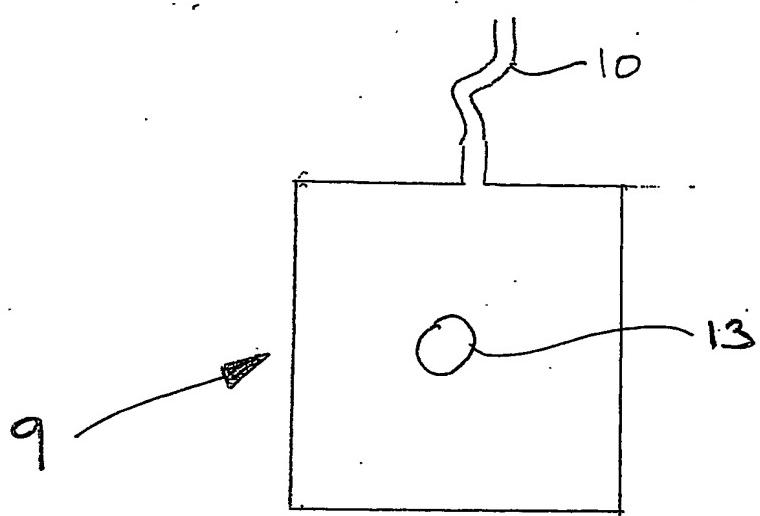


Figure 2

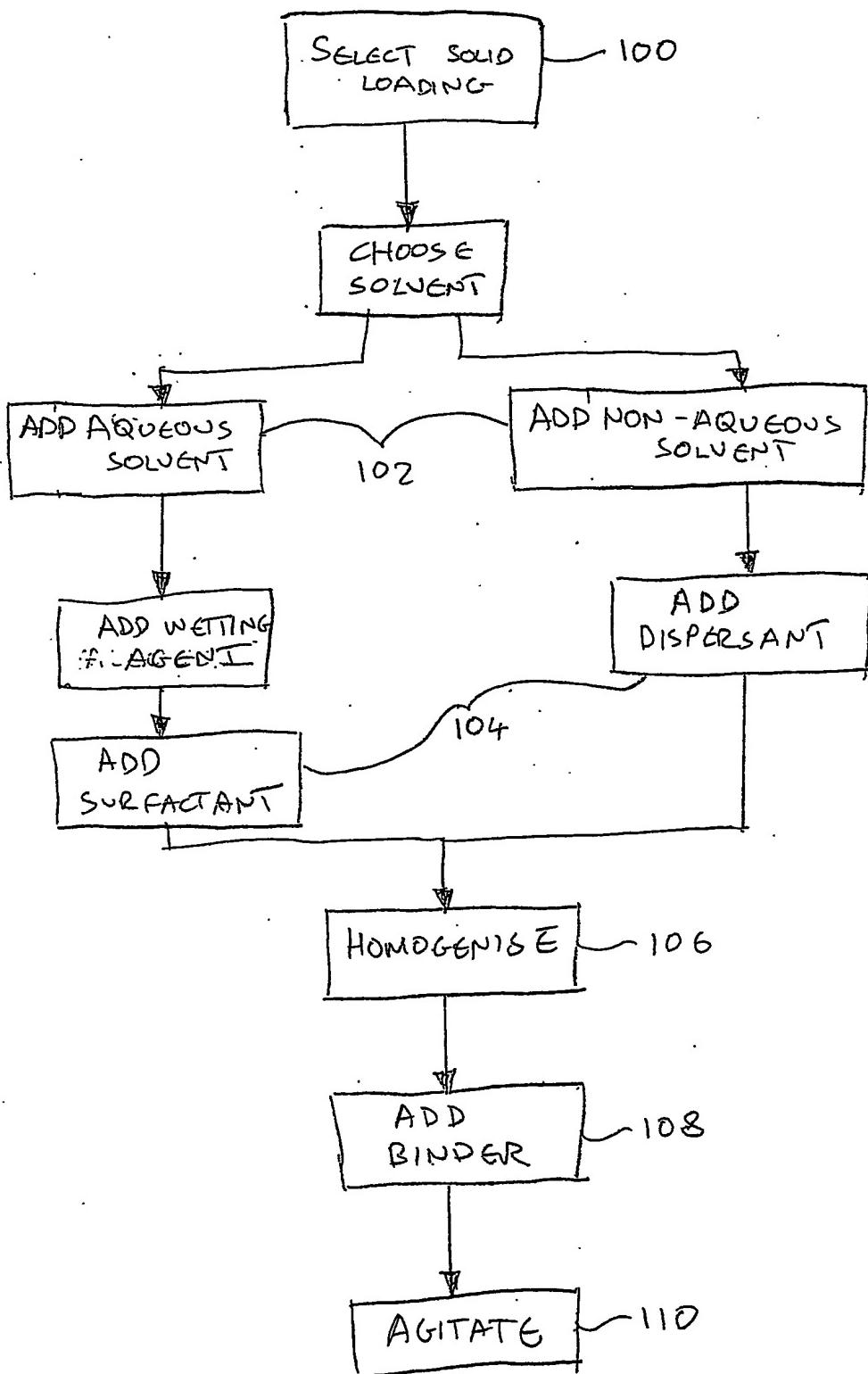


Figure 3

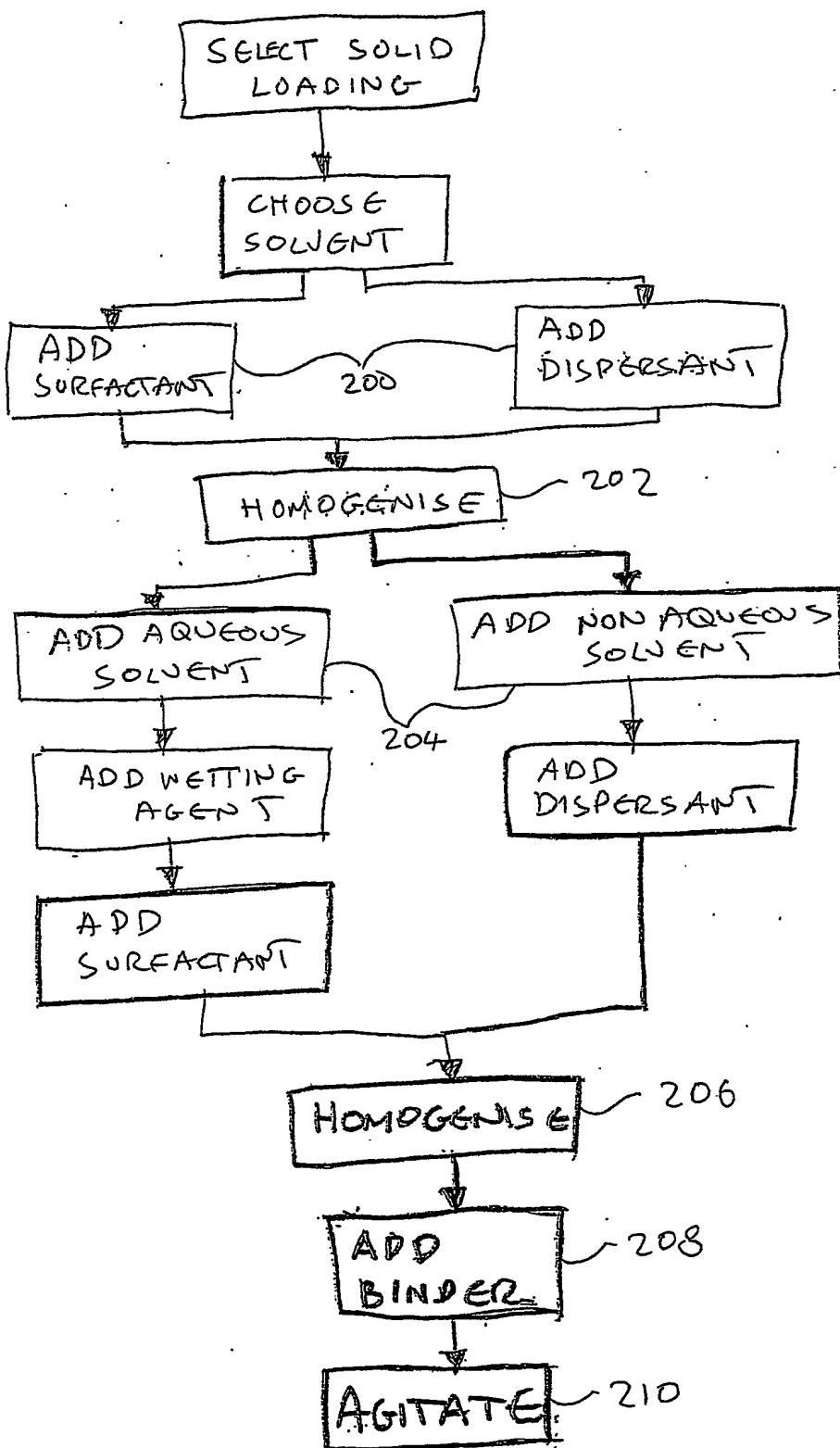


Figure 4

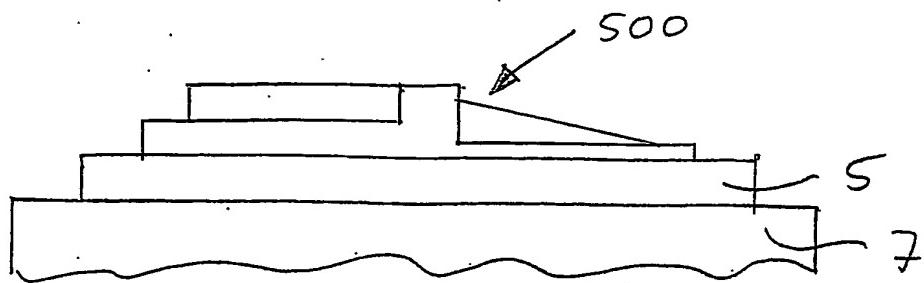


figure 5a

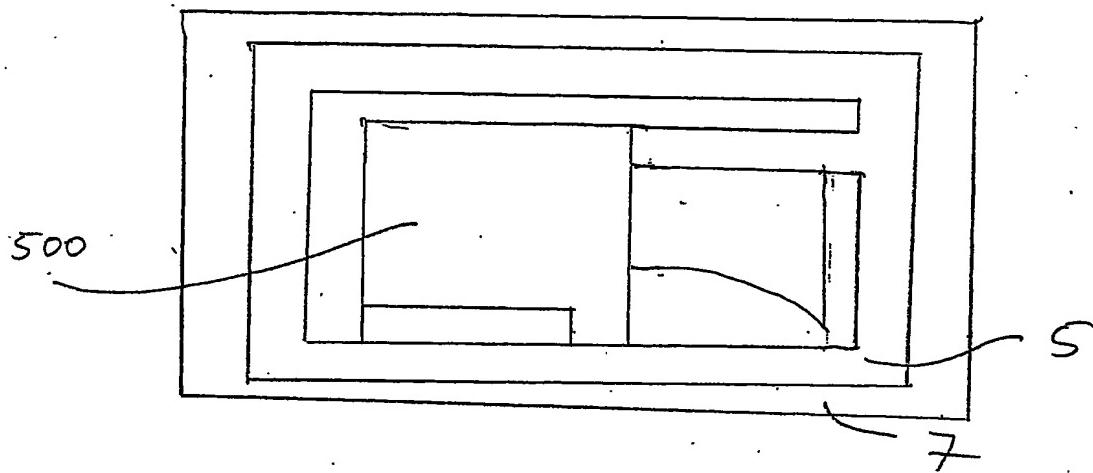


Figure 5b

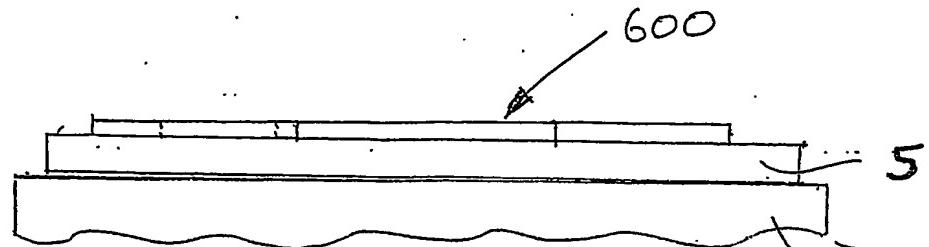


Figure 6a

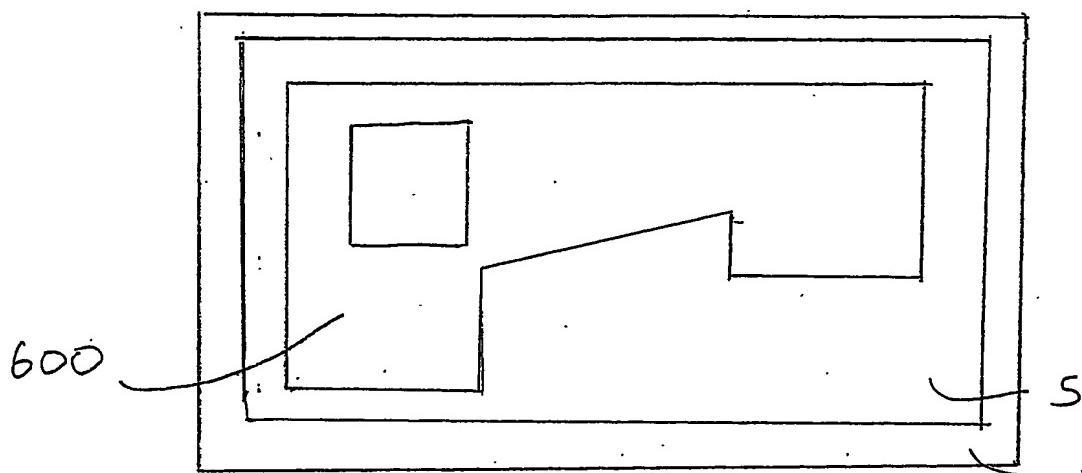


Figure 6b

